

# (12) UK Patent Application (19) GB (11) 2 043 083 A

(21) Application No 7907837  
(22) Date of filing  
6 Mar 1979

(43) Application published  
1 Oct 1980

(51) INT CL<sup>3</sup> C08L 71/04  
C08K 5/53  
(C08L 71/04 25/06)

(52) Domestic classification  
C3R 36C C12 C13P C23  
C8P L1B L4C  
C3K 201 252 EC  
C3Y B262 B263 B270  
F112

(56) Documents cited

None

(58) Field of search  
C3R

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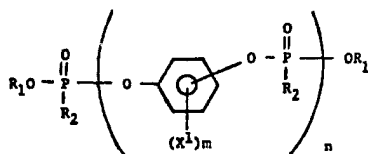
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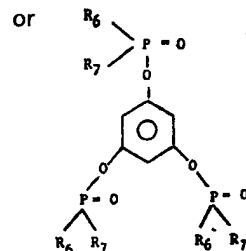
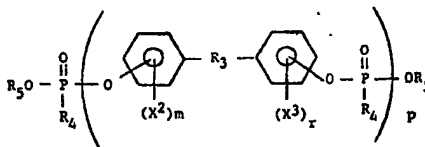
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## (54) Flame retardant polyphenylene ether compositions

(57) There are provided flame retardant thermoplastic compositions suitable for molding, the compositions comprising a normally flammable polyphenylene ether resin, with or without a styrene resin, and a flame retardant amount of a flame retardant agent having the formula:



or



or mixtures thereof, wherein  $R_1$ ,  $R_3$  and  $R_5$  are, independently, hydrocarbon,  $R_2$ ,  $R_4$ ,  $R_6$  and  $R_7$  are, independently, hydrocarbon or hydrocarbonoxy,  $X^1$ ,  $X^2$  and  $X^3$  are halogen,  $m$  and  $r$  are 0 or integers from 1 to 4 and  $n$  and  $p$  are from 1 to 30. In Examples bisphenol-A bisphosphate, bisphenol-A polyphosphate and hydroquinone bisphosphate and added to poly(2,6-dimethyl-1,4-phenylene)ether alone and blended with a rubber-modified high-impact polystyrene.

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## SPECIFICATION

## Flame retardant polyphenylene ether compositions

5 This invention relates to flame retardant polyphenylene ether compositions, and more particularly, to polyphenylene ether compositions which include novel flame retardant agents selected from among certain di- and polyfunctional phosphorus compounds. In comparison with corresponding compositions based on the use of mono-functional, low molecular weight phosphorus containing flame retardant agents, such as triphenyl phosphate, the compositions of this invention provide higher heat deflection temperatures, as well as enhancements in other properties not related to flame retardancy such as tensile strength and plate-out resistance.

*Background of the Invention.*—The use of thermoplastic materials in the formation of shaped articles by compression molding, extrusion, blow molding, and the like is well known. Of particular interest herein are the polyphenylene ether resins, alone or in combination with styrene resins. The polyphenylene ether resins are described, for instance, in Hay, U.S. 3,306,874 and 3,306,875 and in Stamatoff, U.S. 3,257,357 and 3,257,358, the disclosures of which are incorporated herein by reference. Compositions comprising a polyphenylene ether resin in combination with a styrene resin, modified or unmodified, are disclosed in Cizek, U.S. 3,383,453, incorporated herein by reference. Such thermoplastic compositions are known to be moldable to shaped articles having good overall properties.

A major shortcoming in the use of many thermoplastic resins, including polyphenylene ether resins and styrene resins, is their normally flammable nature. In applications where flame resistance is desired, such as in the fields of home construction, automobile and aircraft manufacture, packaging, electrical equipment, furniture, upholstery, and the like, to name just a few, flame extinguishing or retardant agents and/or drip retardant agents are commonly employed with the normally flammable thermoplastic resin or resins.

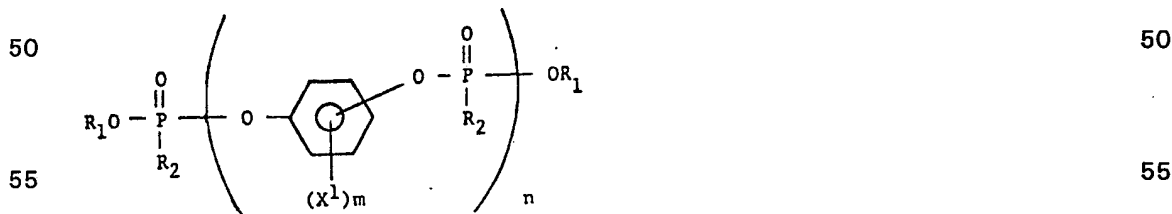
The uses of various antimony-, halogen-, phosphorus-, and nitrogen-containing compounds as flame retardant agents for flammable thermoplastic resins have been proposed in the art. For instance, the use of aromatic phosphates, such as triphenyl phosphate, as such or modified with other compounds, e.g., a halogenated aromatic, as a flame retardant for polyphenylene ether resins has been proposed.

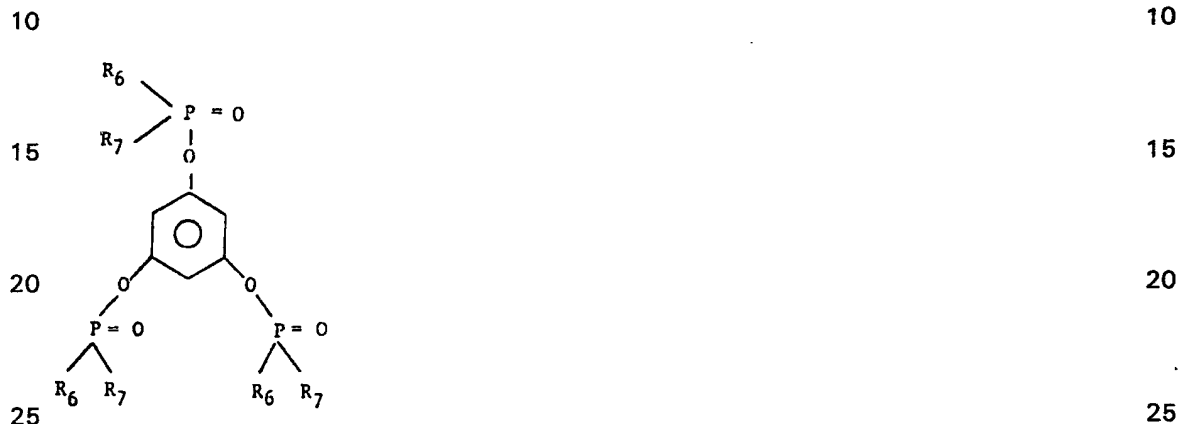
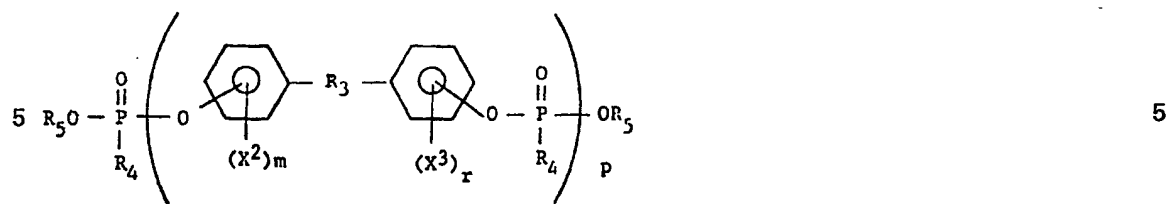
It has now been discovered that certain di- and polyfunctional phosphorus containing compounds are useful as flame retardant agents in compositions comprising a polyphenylene ether resin with or without a styrene resin. Besides being flame retardant, the compositions of this invention provide unexpected enhancements in other properties such as heat deflection temperature, tensile strength and plate-out resistance.

The increased resistance to plate-out provided by this invention is especially noteworthy. "Plate-out" as used in the art refers to the tendency of many flame retardant agents to migrate to the surface of the molten resin during molding. In such instances, the flame retardant agent often adheres to the inside surface of the mold which, in turn, necessitates frequent stoppages for cleaning. With the compositions of this invention, the incidence of plate-out is sharply reduced and molding equipment can be used for longer periods of time without cleaning.

*Description of the Invention.*—In its broadest aspects, this invention comprises flame retardant thermoplastic compositions which comprise:

- (a) a normally flammable polyphenylene ether resin with or without a styrene resin; and  
(b) a flame retardant amount of a flame retardant agent selected from the group consisting of di- and poly-functional phosphate compounds having the general formulae:





and mixtures thereof, wherein  $R_1$ ,  $R_3$  and  $R_5$  are, independently, hydrocarbon,  $R_2$ ,  $R_6$ ,  $R_6$  and  $R_7$  are, independently, hydrocarbon or hydrocarboxy,  $X^1$ ,  $X^2$  and  $X^3$  are halogen,  $m$  and  $r$  are 0 or integers from 1 to 4, and  $n$  and  $p$  are from 1 to 30.

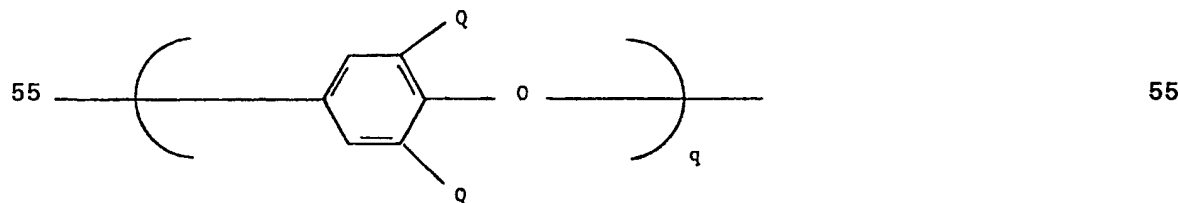
30 As used herein, the term "normally flammable" defines materials which do not meet the V-1 requirement of the Underwriters' Laboratories Bulletin No. 94 flame test. 30

Preferably, within the above general formulae,  $R_1$  and  $R_5$  are, independently, phenyl or alkyl of from 1 to 6 carbon atoms,  $R_3$  is phenylene or alkylidene of from 1 to 6 carbon atoms, and  $R_2$ ,  $R_4$ ,  $R_6$  and  $R_7$  are, independently, phenyl, alkyl of from 1 to 6 carbon atoms, phenoxy or alkoxy of from 1 to 6 carbon atoms. 35

The flame retardant agents of this invention can be prepared using known techniques, starting with commercially available materials. In general, they are prepared by reacting a halogenated phosphate compound with a phenol until the desired number of phosphate functional units are obtained. Under such conditions, the ratio of the phenol to halogenated phosphate compound will determine the number of repeating phenol-phosphate units, the greater the stoichiometric excess of phenol to halogenated phosphate compound resulting in a higher number of repeating units. 40

The phenols can be selected from among a wide variety of dihydric and trihydric phenolic compounds. By way of illustration, these include dihydroxyaromatic compounds such as hydroquinone(1,4-dihydroxybenzene), resorcinol(1,3-dihydroxybenzene), 2,2-bis(4-hydroxyphenyl)propane [bisphenol-A], 2,2-bis(4-hydroxyphenyl)pentane, 3,3-bis(4-hydroxyphenyl)pentane, 1,1-bis(4-hydroxyphenyl)ethane, and the like, and trihydroxy-aromatic compounds such as pyrogallol(1,2,3-trihydroxybenzene) and phloroglucinol(1,3,5-trihydroxybenzene). 45

The normally flammable polyphenylene ether resin is preferably of the type having the structural formula: 50



60 wherein the oxygen ether atom of one unit is connected to the benzene nucleus of the next adjoining unit,  $q$  is a positive integer and is at least 50, and each  $Q$  is a monovalent substituent selected from the group consisting of hydrogen, halogen, hydrocarbon radicals free of a tertiary alpha-carbon atom, halohydrocarbon radicals having at least two carbon atoms between the halogen atom and the phenyl nucleus, hydrocarboxy radicals and halohydrocarboxy radicals 65

having at least two carbon atoms between the halogen atom and the phenyl nucleus.

A more preferred class of polyphenylene ether resins for the compositions of this invention includes those of the above formula wherein each Q is alkyl, most preferably, having from 1 to 4 carbon atoms. Illustratively, members of this class include poly(2,6-dimethyl-1,4-phenylene)ether; poly(2-methyl-6-ethyl-1,4-phenylene)ether; poly(2-methyl-6-propyl-1,4-phenylene)ether; poly(2,6-dipropyl-1,4-phenylene)ether; poly(2-ethyl-6-propyl-1,4-phenylene)ether; and the like.

Especially preferred is poly(2,6-dimethyl-1,4-phenylene)ether, preferably having an intrinsic viscosity of about 0.45 deciliters per gram (dl./g.) as measured in chloroform at 30°C.

The preparation of the polyphenylene ether resins is described in the aforementioned Hay and Stamatoff patents.

The preferred styrene resins will be those having at least 25% by weight of repeating units derived from a vinyl aromatic compound of the formula:



wherein  $\text{R}_8$  is hydrogen, (lower) alkyl or halogen; Z is vinyl, hydrogen, halogen or (lower) alkyl; and t is 0 or an integer of from 1 to 5. Herein, the term "(lower) alkyl" means alkyl of from 1 to 6 carbon atoms.

The term "styrene resin" as used broadly throughout this disclosure includes, by way of example, homopolymers such as polystyrene and polychlorostyrene as well as polystyrenes which have been modified by natural or synthetic rubber, e.g., polybutadiene, polyisoprene, butyl rubber, EPDM rubber, ethylenepropylene copolymers, natural rubber, polysulfide rubbers, polyurethane rubbers, epichlorohydrin, and the like, styrene containing copolymers such as the styrene-acrylonitrile copolymers (SAN), styrene-butadiene copolymers, styrene-maleic anhydride copolymers, styrene-acrylonitrile-butadiene terpolymers (ABS), poly- $\alpha$ -methylstyrene, copolymers of ethylvinylbenzene and divinylbenzene, and the like; block copolymers of the A-B-A and A-B type wherein A is polystyrene and B is an elastomeric diene, e.g., polybutadiene, radial teleblock copolymers of styrene and a conjugated diene, acrylic resin modified styrene-butadiene resins and the like, and blends of homopolystyrene and copolymers of the aforementioned type.

The polyphenylene ether resin and styrene resin are combinable in all amounts.

The amount of flame retardant component (b) is not critical, so long as it is present in a minor, effective amount based on the weight of the resinous components—major proportions may detract from physical properties. In general, amounts from about 1 to about 30, preferably from about 5 to about 15 parts by weight of component (b), based on the weight of components (a), are employed.

The compositions of the invention can also further include reinforcing agents, preferably fibrous glass reinforcements, alone or in combination with non-glass reinforcing fillers. The fibrous glass is, especially preferably, fibrous glass filaments comprised of lime-aluminum borosilicate glass which is relatively soda free, known as "E" glass. However, other glasses are useful where electrical properties are not so important, e.g., the low soda glass known as "C" glass. The filaments are made by standard processes, e.g., by steam or air blowing, flame blowing and mechanical pulling. The preferred filaments for plastics reinforcement are made by mechanical pulling. The filament diameters range from about 0.000112 to 0.00075 inch, but this is not critical to the present invention.

In general, best properties will be obtained if the sized filamentous glass reinforcements comprise from about 1 to about 80% by weight based on the combined weight of glass and polymers and preferably, from about 10 to about 50% by weight. Especially preferably, the glass will comprise from about 10 to about 40% by weight based on the combined weight of glass and resin. Generally, for direct molding use, up to about 50% of glass can be present without causing flow problems. However, it is useful also to prepare the compositions containing substantially greater quantities, e.g., up to 70 to 80% by weight of glass. These concentrates can then be custom blended with blends of resins that are not glass reinforced to provide any desired glass content of a lower value.

Other ingredients, such as stabilizers, pigments, plasticizers, antioxidants, drip retardant agents, and the like, can be added for their conventionally employed purposes.

The manner in which the present compositions are prepared is not critical and conventional methods can be employed. Preferably, however, each of the ingredients is added as part of a blend premix, and the latter is passed through an extruder, at an extrusion temperature of from about 450 to about 600°F., dependent on the needs of the particular composition. The strands

emerging from the extruder may be cooled, chopped into pellets and molded to any desired shape.

*Description of the Preferred Embodiments.*—The following examples are illustrative of the compositions of this invention. They are not intended to limit the invention in any manner.

#### EXAMPLES 1-2

Flame retardant compositions according to this invention are prepared by tumbling 60 parts by weight of poly(2,6-dimethyl-1,4-phenylene)ether, having an intrinsic viscosity of 0.45 deciliters per gram in solution in chloroform at 30°C., 40 parts by weight of a styrene resin (FG 834, Foster-Grant Co., a small rubber-particle high impact polystyrene), 1.5 parts by weight of polyethylene, 0.5 part by weight of tridecylphosphite, 0.15 part by weight of zinc sulfide, 0.15 part by weight of zinc oxide and 12 parts by weight of a flame retardant agent as shown in Table 1, passing the blend through a 28 mm Werner-Pfleiderer twin screw extruder set at 580°F., with 20-25 inch-Hg vacuum-venting, and injection molding the extrudate on a 3 oz. Newbury machine at a cylinder temperature of 525°F. (set) and a mold temperature of 190°F. (set).

For purposes of comparison, a composition according to the prior art is prepared using the same ingredients in the same amounts, except that triphenyl phosphate is used as the flame retardant agent.

The molded compositions are evaluated for physical properties according to ASTM standards and for flame retardancy using the U.L. Bulletin No. 94 flame test. The results are summarized in Table 1.

TABLE 1. Flame Retardant Compositions Comprising a Polyphenylene Ether Resin, a Rubber-Modified High-Impact Styrene Resin and Flame Retardant Agent

EXAMPLE	1	2	A*
Flame retardant agent	bisphenol-A bisphosphate	bisphenol-A polyphosphate	triphenyl phosphate
<i>Properties</i>			
Heat deflection temp., °F.	237	247	210
UL-94 Self-extinguishing times, sec./sec.			
(a) test specimen size, inches	2/6, 9/1, <1/5	2/5, 1/5, 3/3	—
1/8 × 1/2 × 2 1/2			
(b) test specimen size, inches	3/12, 5/27, 4/6, 5/15, 15/3	11/13, 8/26, 9/8, 5/5, 10/11	3/2, 3/8, 1/7, 9/6, 1/2
1/16 × 1/2 × 5			
Notched Izod impact strength, ft.lbs./in.n.	4.8	4.9	6.6
Tensile elongation, %	72	97	55
Tensile strength at yield, psi	10,400	10,400	8,400
Tensile strength at break, psi	9,000	10,000	8,000

\* comparison experiment

#### EXAMPLE 3

Using the procedure described in Examples 1-2, a flame retardant composition comprising 60 parts by weight of poly(2,6-dimethyl-1,4-phenylene)ether, intrinsic viscosity 0.45 dl/g in chloroform at 30°C., 40 parts by weight of a rubber modified high impact styrene resin (FG 834, Foster-Grant Co.), 12 parts by weight of bisphenol-A bisphosphate flame retardant agent, 1.5 parts by weight of polyethylene, 0.5 parts by weight of tridecylphosphite, 0.15 part by weight of zinc sulfide, 0.15 part by weight of zinc oxide and 0.5 part by weight of carbon black.

For comparison purposes, a composition according to the prior art is prepared using the same ingredients in the same amounts, except that triphenyl phosphate is used as the flame retardant agent. The physical properties of the compositions are summarized in Table 2.

TABLE 2. Flame Retardant Compositions Comprising a Polyphenyl ne Ether Resin, a Rubber Modified High Impact Styrene Resin and a Flame Retardant Agent

5	EXAMPLE	3	B*	5
	Flame retardant agent	bisphenol-A bisphosphate	triphenyl phosphate	
	<i>Properties</i>			
10	Heat deflection temp., °F.	239	204	10
	UL-94 Self-extinguish- ing times, sec./sec.			
	(a) test specimen	7/10, 7/17,	2/6, 2/4,	
15	size, inches	16/9, 5/9,	2/4, 2/2,	15
	1/16 × 1/2 × 5	6/2	6/3	
	Tensile elongation, %	69	84	
	Tensile strength at yield, psi	9,500	7,500	
20	Tensile strength at break, psi	8,300	7,100	20
	Degree of Plate-out	Light (sig- nificantly less than comparison experiment)	Heavy	
25				25

\* comparison experiment

- 30 The "degree of plate-out" is determined by injection molding fifteen consecutive "short-  
shots" (the molding material is allowed to only partially fill the mold) under the specified  
molding conditions. A "full shot" is run immediately after the short-shot, in order to pick up the  
"plated-out" flame retardant residue deposited on the inside surface of the mold. The molding  
temperatures are 580°F. (cylinder) and 180°F. (mold); the total molding cycle is 40 seconds  
35 from injection to removal of the part from the mold. The molded part is a plaque having the  
dimensions 1/8 inch × 3 inches × 6 inches. 35

#### EXAMPLES 4-5

- 40 Flame retardant compositions according to this invention are prepared by forming a preblend  
of the ingredients, passing the blend through a 28 mm Werner-Pfleiderer twin-screw extruder  
set at 500-540°F., with no vacuum-venting, and injection molding extrudate on a 3 oz.  
Newbury molding machine at 540°F. (set) cylinder temperature and 190°F. (set mold tempera-  
ture. 40

- 45 The ingredients and physical properties of the respective compositions are summarized in  
Table 3. 45

TABLE 3. Flame Retardant Compositions Comprising a Polyph nyl ne Ether R sin and a Flame Retardant Agent

5	EXAMPLE	4	C*	5	D*	5
	Ingredients, parts by weight					
10	poly(2,4-dimethyl- 1,4-phenylene) ether	75	75	85	85	10
	bisphenol-A-bis- phosphate	25	—	15	—	
	triphenylphosphate	—	25	—	15	
15	Properties					15
	Heat deflection temp., °F.	250	205	289	267	
	UL-94 Self-extinguish- ing times, sec./sec.					
20	(b) test specimen size, inches	1/3, 2/4, 1/3, 1/3, 2/3	0/2, 1/1, 0/3, 1/3, 0/2	6/3, 1/6, 3/5, 1/4, 1/2	1/3, 0/2, 1/2, 1/4, 0/3	20
	Izod impact strength, ft.lbs./in.n.	0.6	0.7	0.8	1.1	
25	Tensile elongation, %	25	93	37	78	25
	Tensile strength at yield, psi	13,600	9,500	13,100	11,500	
	Tensile strength at break, psi	9,700	9,500	9,800	11,300	
30						30

\* comparison experiment

#### EXAMPLE 6

A flame retardant composition according to this invention is prepared by forming a pre-blend  
 35 of 55 parts by weight of poly(2,6-dimethyl-1,4-phenylene)ether, intrinsic viscosity 0.45 dl/g. in  
 chloroform at 30°C., 45 parts by weight of a rubber modified high impact polystyrene (FG 834,  
 Foster-Grant Co.), 4 parts by weight of hydroquinone bisphosphate flame retardant agent, 1.5  
 parts by weight of polyethylene, 1.0 part by weight of tridecylphosphite 0.15 part by weight of  
 40 zinc sulfide and 0.15 part by weight of zinc oxide, passing the blend through a 28 mm Werner-  
 Pfleiderer twin-screw extruder at 575°F., with 25 in.-Hg vacuum venting, and injection molding  
 the extrudate on a 3 oz. Newbury machine at 530°F. (set) cylinder temperature and 190°F. (set)  
 mold temperature.

For purposes of comparison, a corresponding prior art composition using triphenyl phosphate  
 as the flame retardant agent is also prepared and molded using the same conditions. The  
 45 physical properties of the respective compositions are summarized in Table 4.

TABLE 4. Flame Retardant Compositions Comprising a Polyphenylene Ether Resin, Rubber Modified High Impact Styrene Resin and a Flame Retardant Agent

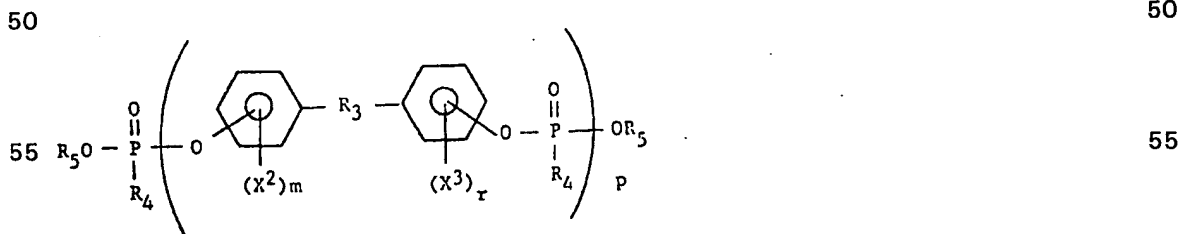
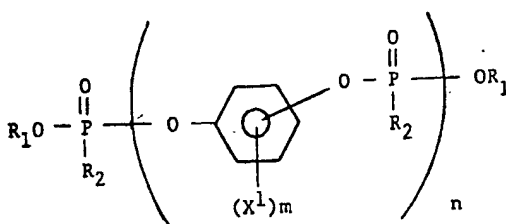
5	EXAMPLE	6	E*	5
	Flame retardant agent	hydroquinone-bisphosphate	triphenylphosphate	
	<i>Properties</i>			
10	Heat deflection temp., °F.	251	242	10
	UL-94 Self-extinguishing times, sec./sec.			
15	(a) test specimen size, inches	9/6, 6/8, 14/15, 10/7, 16/8	4/9, 14/11, 21/6, 7/5, 17/15	15
	1/8 × 1/2 × 2 1/2			
	Izod impact strength, ft.lbs./in.n.	2.7	3.8	
	Tensile elongation, %	58	93	
20	Tensile strength at yield, psi	10,300	9,400	20
	Tensile strength at break, psi	8,900	9,100	
25	* comparison experiment			25

Obviously, other modifications and variations of the present invention are possible in the light of the above disclosure. It is, therefore, to be understood that changes may be made in the particular embodiments described above which are within the full intended scope of the invention as defined in the appended claims.

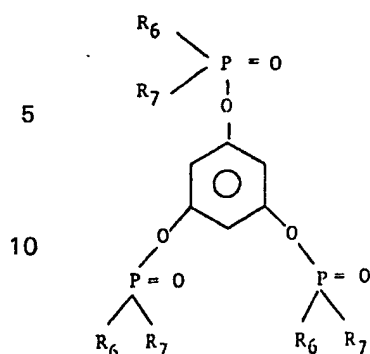
#### CLAIMS

1. A flame retardant thermoplastic composition which comprises:

- (a) a normally flammable polyphenylene ether resin with or without a styrene resin, and  
(b) a flame retardant amount of a flame retardant agent selected from the group consisting of di- and polyfunctional phosphate compounds having the general formula:







and mixtures thereof, wherein  $R_1$ ,  $R_3$  and  $R_5$  are, independently, hydrocarbon,  $R_2$ ,  $R_6$  and  $R_7$  are, independently, hydrocarbon or hydrocarboxy,  $X^1$ ,  $X^2$  and  $X^3$  are halogen,  $m$  and  $r$  are 0 or integers from 1 to 4, and  $n$  and  $p$  are from 1 to 30.

2. A composition as defined in Claim 1 wherein  $R_1$  and  $R_5$  are, independently, phenyl or alkyl of from 1 to 6 carbon atoms,  $R_3$  is phenylene or alkylidene of from 1 to 6 carbon atoms, and  $R_2$ ,  $R_6$  and  $R_7$  are, independently, phenyl, alkyl of from 1 to 6 carbon atoms, phenoxy or alkoxy of from 1 to 6 carbon atoms.

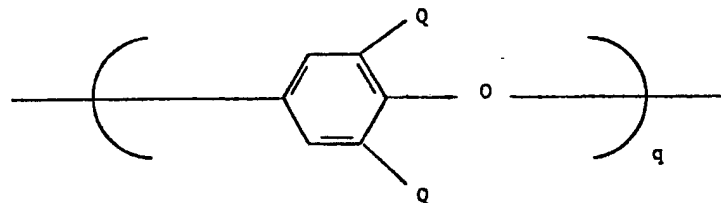
3. A composition as defined in Claim 1 wherein said flame retardant agent is bisphenol-A bisphosphate.

4. A composition as defined in Claim 1 wherein said flame retardant agent is bisphenol-A polyphosphate.

5. A composition as defined in Claim 1 wherein said flame retardant agent is hydroquinone bisphosphate.

6. A composition as defined in Claim 1 wherein said flame retardant agent is present in an amount of from about 1 to about 30 parts of (a).

7. The composition of Claim 1 wherein the polyphenylene ether resin of (a) has the formula:



wherein the oxygen ether atom of one unit is connected to the benzene nucleus of the next adjoining unit,  $q$  is a positive integer and is at least 50, and each  $Q$  is a monovalent substituent selected from the group consisting of hydrogen, halogen, hydrocarbon radicals free of a tertiary alpha-carbon atom, halohydrocarbon radicals having at least two carbon atoms between the halogen atom and the phenyl nucleus, hydrocarboxy radicals and halohydrocarboxy radicals having at least two carbon atoms between the halogen atom and the phenyl nucleus.

8. The composition of Claim 7 wherein the polyphenylene ether resin is poly(2,6-dimethyl-1,4-phenylene)ether.

9. The composition of Claim 1 wherein a styrene resin is present.

10. The composition of Claim 9 wherein the styrene resin is a rubber modified high impact polystyrene.

11. The composition of Claim 1 which includes a reinforcing amount of a reinforcing filler.

12. A composition as defined in Claim 1 and substantially as hereinbefore described with reference to any of Examples 1 to 6.